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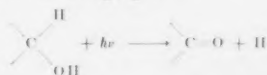
Degradation of Cellulose by Ultraviolet Light

TO PROVIDE basic information on the properties of paper, the Bureau is investigating the primary processes that occur when cellulose molecules are broken down by ultraviolet light. In recent experiments, the rate of evolution of gaseous products during exposure was measured. The results indicate that the main reaction in the far ultraviolet region is the decomposition of the alcohol groups in the cellulose to produce carbonyl groups as hydrogen gas is evolved.¹ Data from these experiments should be of considerable value in determining more desirable conditions for the preservation and storage of records and the display of historical documents.

Cellulose, the most abundant organic compound found on the earth's surface, is the raw material for many textiles and plastics as well as for paper goods. A cellulose fiber is a partially crystalline mass of long chain-like molecules composed of up to 10,000 units of glucose joined together by oxygen atoms. In a cellulose chain of N glucose units, there are $3N+1$ hydroxyl groups, $N-1$ oxygen links between glucose units, one aldehyde group, and occasional carbonyl, other aldehyde, and carboxyl groups, any of which may be decomposed by ultraviolet light.

In the present study, which was carried out by Bureau scientists J. H. Flynn, W. K. Wilson, and W. L. Morrow, the gases evolved were approximately 90-percent hydrogen and 10-percent carbon monoxide and carbon dioxide. The evolution of hydrogen upon irradiation of cellulose with 2537-A light does not seem to have been previously noted in the literature; it was

found to follow a parabolic rate law indicating inhibition by a product. A plausible explanation of the source of hydrogen is the photolysis of alcohol groups by the over-all reaction as shown in the following equation, where h is Planck's constant and ν is the frequency of the irradiating light:



This reaction is known to occur when liquid alcohols are irradiated at approximately 2000 Å.

An equation was developed for calculating the number of chain fractures in the photochemical degradation of solids. Application of this equation to data derived from the experiments showed that a close parallel existed between amounts of carboxyl formed and the calculated number of chain fractures, indicating that these reactions may be related.

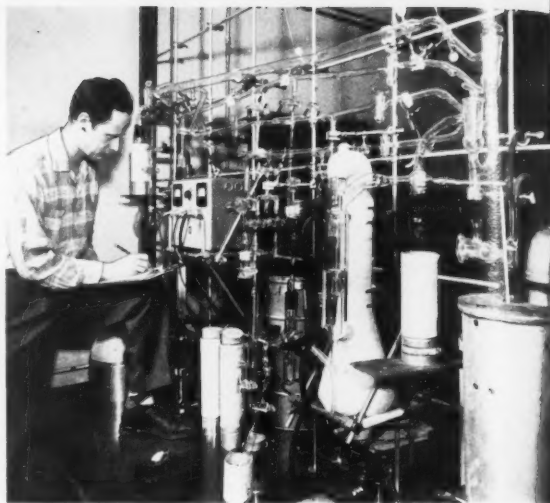
For the present investigation, purified, dried, cotton cellulose was irradiated in an evacuated system with 2537-Å light. The cellulose was made into sheets on a handsheet machine, and cut into rectangles of 92 cm², 0.0018 cm thick, and weighing 0.86 g. A cellulose sheet was placed around a "cold finger" of Pyrex glass through which water from a constant-temperature bath was circulated. The cold finger was sealed into a large quartz tube that was inserted axially into an etched cylindrical aluminum reflector. A stopcock connected the quartz tube to a vacuum manifold and to the various measuring instruments.

The cellulose was irradiated by five low-pressure mercury lamps set vertically at even intervals around the inside surface of the aluminum reflector. The operating temperature of the lamps was maintained at $40^\circ \pm 1^\circ \text{C}$ by an airblower fitted into the top of the reflector so that the energy in the ultraviolet region resulted almost entirely from the 2537-A Hg line. Intensity of the irradiating light was determined by means of a sensing device that had been calibrated against a standard source in the Bureau's radiometry laboratory.

The pressure of evolved gas was measured by a thermocouple gage, a discharge gage, and a mercury manometer. Composition of gaseous products was determined with a mass spectrometer. The irradiation apparatus and reaction vessel assembly permitted the gases to be rapidly removed to a collection point, thus preventing complicating interactions with highly reactive residues that remained attached to the solid.

Investigations are continuing at the Bureau to obtain further information on the mechanisms of this important degradative reaction. Data compiled from the cumulative studies will be used to devise and evaluate methods for making paper more stable on exposure to light.

¹ For further technical details, see Degradation of cellulose in a vacuum with ultraviolet light, by Joseph H. Flynn, William K. Wilson, and William L. Morrow, *J. Research NBS* **60**, 229 (1958) RP2841.



Apparatus for investigating the degradation of cellulose by ultraviolet light. Scientist takes pressure readings from a thermal conductivity gage on the left. On the extreme right is the cylindrical aluminum reflector containing the reaction vessel and irradiation apparatus.

Audiofrequency Voltammeter

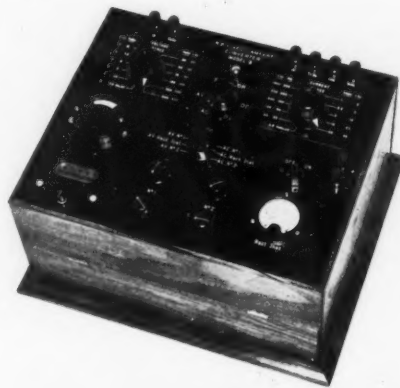
ACCURATE voltage and current measurements are now possible over a frequency range from 5 to 50,000 cps with a self-contained, portable volt-ampere converter recently developed at the Bureau. The increasing use of audiofrequencies, especially in airborne devices, has made necessary the development of special equipment and transfer standards for tests of instruments operating in this range. As the primary electrical units are maintained by d-c standards, all a-c measurements of voltage, current, and power are actually based on transfer instruments, which are standardized on dc and then used on ac.

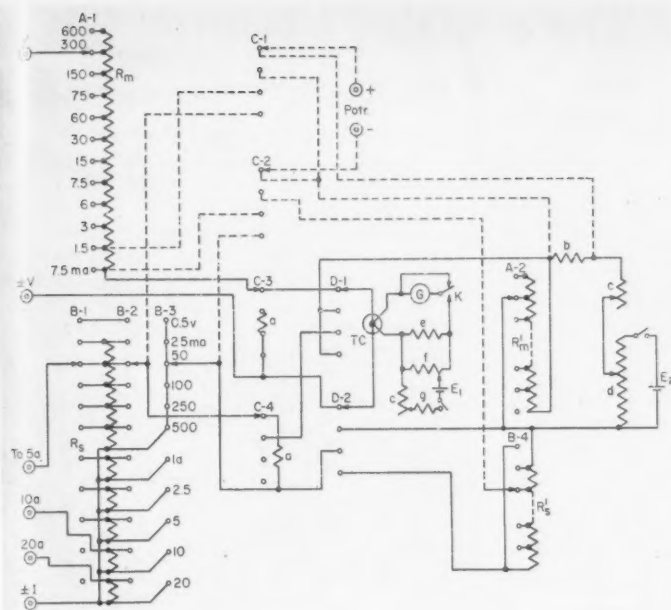
Based on an earlier and more limited prototype,¹ the present instrument was designed and constructed by F. L. Hermach and E. S. Williams of the electrical instruments laboratory for the Bureau's Electronic Calibration Center² at Boulder, Colo. Among other changes, 12 voltage ranges from 0.5 to 600 v and 11 current ranges between 7.5 and 20 amp are now available. These ranges may be used either for d-c or a-c measurements with a 1.5-v potentiometer or for a-c—d-c transfer tests of instruments.

Like other transfer instruments for accurate standardization at the higher audiofrequencies, the improved voltammeter utilizes a thermal converter as the sensitive component.³ A thermal converter consists essen-

tially of a conductor, heated by the ac to be measured, and a thermocouple, thermally attached near the center of the heater. The heater of the converter is connected in series with appropriate resistors for voltage measurements and in parallel with appropriate shunts for current measurements. The output electromotive force

Assembled volt-ampere converter used for calibrating instruments at audiofrequencies. The converter gives accurate values of voltage and current over the range from 5 to 50 kc.





Wiring diagram of the volt-ampere converter for use in audiofrequency calibration work. Switch A controls series resistors R_m and compensating resistors R'_m . Switch B controls shunt resistors R_s and compensating resistors R'_s . C is the function selector switch. F is the thermal converter transfer switch. Shown from top to bottom on the diagram are positions on the selector and transfer switches: AV (alternating voltage), AC, DV, and DC are positions on the selector switch: AV No. 1, AV No. 2, AC No. 1, and AC No. 2 are positions on the transfer switch.

produced in the thermocouple is first balanced against the voltage from an internal d-c "bucking circuit" to obtain a null reading on a built-in galvanometer. Then the heater is switched to an internal d-c circuit, which is adjusted to give the same output emf and therefore equivalent heater current and voltage drop. A simple multiplication of the voltage measured across a portion of this d-c circuit yields the unknown alternating voltage or current. The 7.5-ma thermal converter used has excellent transfer characteristics, its a-c—d-c difference being less than 0.01 percent at audio-frequencies.

Changes in heater resistance are compensated by connecting additional resistors in the circuit. In voltage measurements, a resistor equal to the series resistance is placed in parallel with the thermal converter in the d-c position. In current measurements, a resistor equal to the shunt resistance is placed in series with the thermal converter in the d-c position. The accuracy of the instrument is then dependent only on the potentiometer used to measure the voltage and on the highly stable internal resistors.

A function-selector switch is used to connect the thermal converter circuit to the shunts for a-c measurements, and to the series resistors for alternating-voltage measurements. For direct-voltage measurements the 1.5-v section of the series resistors is connected directly to the potentiometer, and for d-c measurements the shunt voltage is connected directly to the potentiometer. This relatively simple switching permits the same resistors and shunts to be used for d-c as well as a-c measurements, thus greatly increasing the usefulness of the instrument.

Binding posts on the panel make possible the inclusion of a milliammeter in the balancing circuit to measure the thermal-converter output voltage. With these data and a converter characteristic curve, a-c—d-c difference tests can be made of voltmeters and ammeters with an accuracy of 0.02 percent. In such tests, the volt-ampere converter is connected in series with the test ammeter, or in parallel with the test voltmeter. Alternating and direct current are then applied successively to the arrangements. By using a more sensitive external galvanometer in place of the built-in galvanometer, the a-c—d-c difference of the test instrument can be obtained.

Special precautions were taken to minimize reactance. High-quality resistance cards were used for the series and shunt resistors of 1 ohm or more. Shunts of lower resistance, for the higher current ranges, were constructed of bifilar strips of Ni-Cr-Al-Fe alloy with insulation of 1-mil polyester film. In addition, rotary switches with enclosed silver contacts were used to give minimum-contact resistance, inductance, and internal capacitance.

¹ Accurate audiofrequency instruments, *NBS Tech. News Bul.* **39**, 47 (April 1955). For further details, see Multirange audio-frequency thermocouple instruments of high accuracy, by F. L. Hermach and E. S. Williams, *J. Research NBS* **52**, 227 (May 1954) RP2494.

² For further information, see Electronics Calibration Center at NBS Boulder Laboratories, *NBS Tech. News Bul.* **41**, 24 (February 1957).

³ Thermal converters as ac-dc transfer standards for current and voltage measurements at audio-frequencies, by F. L. Hermach, *J. Research NBS* **48**, 121 (February 1952) RP2296. Transfer standards for audio-frequency tests, *NBS Tech. News Bul.* **36**, 42 (March 1952).

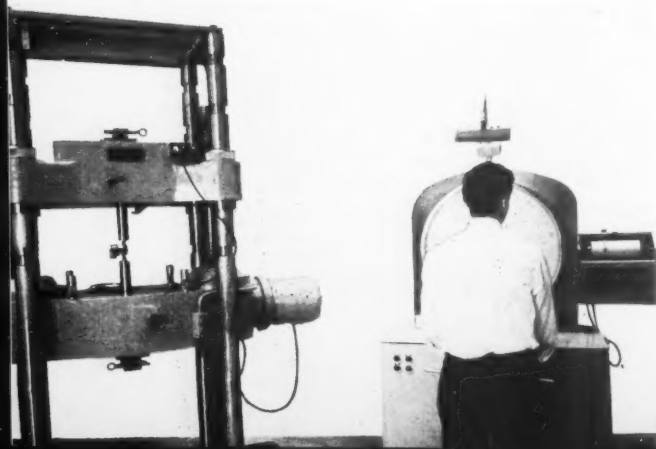
Evaluation of Stress-Strain Recorders

THE BUREAU, in a program of basic instrumentation sponsored by the Department of Defense and the Atomic Energy Commission, has obtained performance data on extensometers and recorders used to determine the properties of metals. The tests, conducted on three types of extensometer-recorder systems in use by testing laboratories throughout the country, indicate that such instruments basically are capable of meeting the requirements of Government and industry. The investigation was aimed at more functional adaptation and more effective use of equipment producing autographic stress-strain records of tensile tests. It included not only calibrations of stress and strain coordinates but the measurement of other characteristics that affect accuracy—such as the expansion of graph paper in humid weather. The procedures¹ developed in this work are being made available to industry to aid in the evaluation and calibration of individual recorders.

Although stress-strain recorders are widely used to determine the mechanical properties of steel, concrete, fabrics, rubber, wood, and plastics, little information is available on their accuracy. However, as recorders find their greatest application in production control—checking the compliance of materials with purchase specifications—accuracy is an important factor. To provide the necessary data on instruments for metals testing, the present investigation was undertaken by R. R. Bouche and D. R. Tate of the Bureau staff.

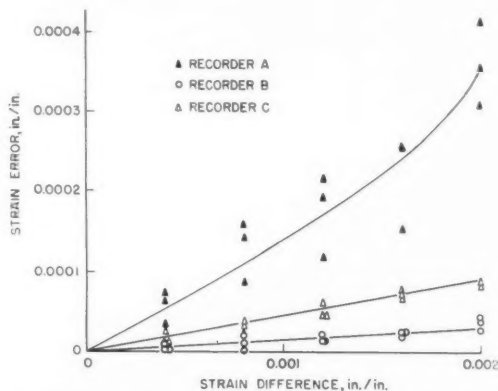
A stress-strain recorder is a highly complex instrument which incorporates several operations in its performance. Essentially it determines certain properties of materials by plotting a curve of stress versus strain on graph paper. The sensing device is an extensometer—an instrument that detects elongation in the test sample and transmits a proportional electrical, mechanical, or optical signal to the recorder. The recorder pen plots the strain proportional to this signal along one coordinate and the stress proportional to the applied load along the other.

Autographic stress-strain recorder in operation. Recorder (extreme right) is in the process of drawing a typical stress-strain diagram of a material under test (at left). The accuracy of such recorders was recently evaluated.



Calibration of Strain Coordinate

Since the extensometer controls the recorder strain readings, a precise determination of its accuracy in measuring length increments is necessary. The Bureau performed such a calibration by using the recorder-extensometer combination and an interferometric comparator simultaneously to measure a given displacement. Since the interferometric arrangement is sensitive to displacements smaller than 0.000001 in., a comparison of the two distances reveals any error in the recorder arrangement.

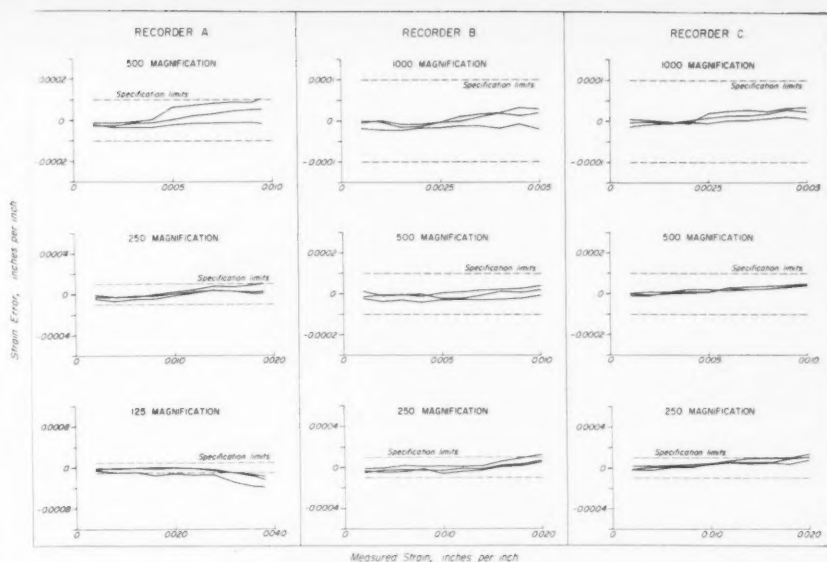


Test results obtained at the Bureau illustrate the ability of extensometers to measure the average of unequal strains.

In the comparison, the increment measured is the displacement of two coaxial bits as they are moved away from each other along their mutual axis. The interferometer and the extensometer are both arranged to measure this movement. As the distance changes, interference fringes are formed in the eyepiece of the interferometer and counted by an attached photoelectric counter. From the number of fringes and the wavelength of the light used (helium source), the actual distance is determined.

To check the accuracy of the strain coordinate itself, the applied strain is compared to the indicated strain on the chart paper. The applied strain is the extension measured by the interferometer divided by the measured gage length of the extensometer which sometimes differs significantly from its nominal gage length. The indicated strain on the chart paper is based on the extensometer's nominal gage length.

Each recorder-extensometer combination was calibrated three times at each of its three magnifications. These were either 125, 250, and 500; or 250, 500, and 1,000. At the higher magnifications, extensometers satisfy more closely the specifications set by the American Society for Testing Materials for Class B extensometers. Class B extensometers are ordinarily used for



Calibration curves showing the performance on the strain-recording axis of three stress-strain recorders. All recorders are seen to correspond more closely to the specification limits (ASTM tolerances for Class B extensometers) at higher magnifications.

determining the modulus of elasticity, yield strength, permanent set, or deviations from Hook's law.

Other inherent characteristics that may further affect recorder accuracy and cause deviation from specification limits are resolution, warm-up time, averaging ability, and load response. Methods of investigating these factors were also devised.

Resolution and Warm-Up Time

In determining the resolution of the recorder, extensometers are subjected to extension at a constant speed. The resolution values are the smallest applied extensions capable of moving the recording pen. They are determined by measuring the extension with the interferometric arrangement described above while the rotation of the drum which moves the pen is observed visually with a microscope.

Another test was conducted to determine how much time is required for the recorder to achieve stability after it is connected to a power supply. In connection with this test, observations are made on the magnitude of drift. The recorder, with extensometers attached, is turned on and the rotation of the drum observed as a function of time. It was found that a short warm-up period is required for the differential-transformer type of recorder but not for the electrical-contact recorder. The warm-up time required with the differential-transformer recorder is probably a result of power dissipation in the transformer windings; additional observations showed that the warm-up time is independent of core position.

Determination of Averaging Ability

A test was introduced to evaluate the effectiveness of extensometers in averaging strain. In the actual testing of materials strain is not equal in all fibers. Therefore, it is necessary to determine the average strain by meas-

uring the extension of two fibers opposite one another on the periphery of the specimen cross section. Special extensometers are available for this type of measurement.

The averaging ability of such extensometers can be evaluated by using them to measure the difference between compressive and tensile strain in a beam subjected to a uniform bending moment. A resistance strain gage is also used to measure this difference. The discrepancy between the strain readings in the two devices is the error in the averaging extensometer. This test showed that the strain errors for the extensometers were less than one-fourth of the strain differences.

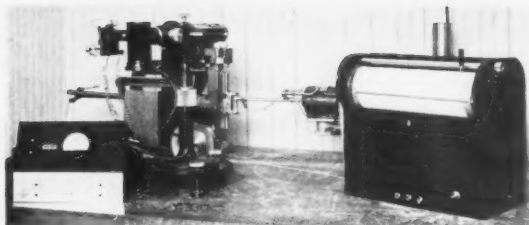
Calibration of the Load Coordinate

The load coordinate is very simply calibrated by mounting a recorder on a testing machine. The recorder is turned off to prevent the drum from rotating, and in this way made to record only the load. The value of this load can be read directly from the testing machine indicator and this value compared with the recorded load. The errors in the recording of load were less than 1 percent except for isolated points at the lowest and highest loads.

In determining the accuracy of load and extension indications of a recorder, the effects of expansion and contraction of chart paper must be eliminated. This was accomplished by measuring the length of the recorder plot directly rather than reading its length from the paper grid. A separate evaluation of the dimensional stability of the paper was also carried out.

Stability of Chart Paper

The effects of relative humidity on the stability of the paper were studied by exposing three samples of chart paper from each recorder to constant relative humidities from 40 to 80 percent. The use of two microscopes



Calibration apparatus used for strain-measuring devices. The equipment employs an interferometer (center) and a photoelectric counter (left) to measure exactly the elongation detected by the extensometer associated with a stress-strain recorder (right).

permitted a comparison of the chart paper with a calibrated steel scale. In this way the expansion and contraction were measured over a 7-in. length at 70° F both with and across the grain. Error introduced by humidity was found to be a significant factor. For example a 40-percent change in relative humidity changed the length of the paper across the grain by 0.6 to 0.7 percent. The uniformity of the grid of the chart paper

was also measured. Each one-tenth of an inch division deviated from the average by less than 0.0004 in.

The results obtained in this study are presumed typical of the performance of the majority of recorders in use, showing the stress-strain recorder to be a reasonably accurate instrument suitable for the type of tests in which it is employed. However, periodic calibration of each recorder-extensometer combination is, of course, necessary to insure the satisfactory performance of which it is capable.

¹ Autographic stress-strain recorders, by Raymond R. Bouche and Douglas R. Tate, *ASTM Bul.* **228**, 33 (February 1958).

Direct-Reading Viscometer

A CONVENIENT, simple, direct-reading viscometer has been developed by M. R. Shafer of the Bureau's combustion controls laboratory for the Navy Bureau of Aeronautics.¹ Designed specifically to measure the kinematic viscosity of liquid in a continuous-flow process, the instrument will be used to obtain data on hydrocarbon fuel in the adjustment and calibration of fuel-metering accessories for aircraft engines.

The development of this viscometer is a result of calibration work² on fuel flowmeters and fuel-metering components for aircraft engines. The precise adjustment and calibration of fuel metering and control components prior to installation is necessary to secure optimum performance in flight. As fuel flow-rate instruments are sensitive to the effects of liquid viscosity, a convenient method of viscosity measurement was in demand.

The direct-reading viscometer has been shown to meet this demand. The usual method for viscosity determinations involves the measurement of the time required for liquid to pass through a capillary, and a subsequent graphical or analytical conversion to viscosity. Such a technique is obviously not suited for continuous indication of viscosity. The present instrument, on the other hand, permits the viscosity to be read from a single manometric column without corrections or calculations.

Essentially, the viscometer consists of two flow restrictions of different configurations, a capillary and an orifice, in series. Manometers are provided for indicating the total loss in head across both restrictions and the loss in head across the downstream restriction only. If the total loss in head is maintained at a constant value when passing different liquids, then the loss in head across the downstream restriction is a direct function of the kinematic viscosity—read directly from a scale calibrated in appropriate units and placed next to the second manometer.

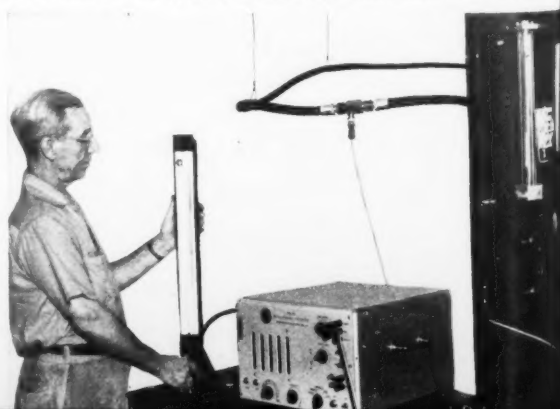
The prototype developed by the Bureau has a range of 0.4 to 5.0 centistokes. This encompasses the viscosity of fuels commonly used by the aviation industry, such as gasoline, naphtha, kerosine, and jet fuels. However, the instrument range may be varied as desired by altering the type and size of the two fixed restrictions.

To within an accuracy of 2 percent, this instrument provides a convenient, rapid measurement of viscosity. It also offers several advantages over other instruments used to monitor continuously the viscosity of flowing fluid, being simple to operate, involving no electronic components, and requiring no power connection. As the direct-reading viscometer provides a sensitive measure of viscosity in the range of 0.2 to 5.0 centistokes, it is applicable to many industrial control and monitoring purposes.

¹ United States Patent No. 2,700,891: A direct-reading viscometer.

² Fuel handling accessories for aircraft, *NBS Tech. News Bul.* **37**, 33 (March 1953).

Direct-reading viscometer is used in calibrating a turbine-type flowmeter (top center). Digital frequency-time counter on table measures output of flowmeter, while calibrating stand (right) accurately determines flow rate.



AUTOMATIC SYSTEM FOR SPECTROMETRIC DATA



AUTOMATIC data-processing equipment now in use at the Bureau is providing almost immediate information on the homogeneity of metals and alloys. By means of a specially designed electronic read-out, analyses obtained on a direct-reading spectrometer are automatically recorded on punched cards in a form that permits high-speed statistical analysis on an electronic computer. As a result, information is obtained in minutes which in the past would have required weeks of work by several operators.

The automatic data-handling system is being employed in an expanded program for the preparation of spectrometric standard samples, which the Bureau distributes for calibration of spectrometers in other laboratories. At present, the Bureau issues over 550 different standard samples of chemicals, metals, ores, and ceramics—all certified materials which have been carefully analyzed or whose physical properties have been precisely determined. However, recent requests from industry have indicated a need for a greatly increased number of spectrometric standard samples. Uniformity of composition is especially important in such materials, so that a rapid means for assessing homogeneity of specimens was needed.

The spectrometer and electronic read-out were designed and built by Baird-Atomic, Inc., in accordance with the Bureau's requirements. The spectrometer provides for analysis in terms of 36 chemical elements, any 18 of which may be observed simultaneously. As in other spectrometers of this type, an electric spark vaporizes a minute portion of the sample, and the light from the spark passes through a slit to a diffraction grating, which disperses the light to form a spectrum. A selected spectral wavelength for each chemical element passes through a slit to a phototube, and the electric current produced by the tube is stored as a charge on a condenser. At the end of the exposure the amount of each element present is measured by the charge on the corresponding condenser.

In the present instrument, the heart of the recording system is a storage unit in which measured charges on condensers are indicated as numbers on glow-tube registers. The end of each glow tube bears a circular scale of digits from 0 to 9 and the measured digit is

Automatic spectrometric equipment recently installed at the Bureau makes possible immediate statistical analysis of spectrometric data. In the storage unit (left background) measurements proportional to the amounts of the various elements present are indicated on the dials of glow-tube registers. The card punch (left foreground) automatically records these data on punched cards for statistical analysis in a high-speed computer.

indicated by the position of a glowing spot in the tube. Four registers, together representing a 4-digit number, constitute a single channel of information, which provides a measurement of the intensity of a spectral line of one of the chemical elements. This electronic read-out system is connected to a card punch so that the data may be automatically recorded on punched cards for input to a high-speed computer.

Operation is fully automatic once the operator has placed the sample in the spectrometer and pushed the starting button. The spectral exposure is made in about 30 sec; the measurements of spectral line intensities are read into the storage unit in 5 sec and are punched in a card 5 sec later. For a set of about 30 samples tested, the resulting punched cards are transferred to the computer, which has been programed previously to receive and process the data. In 3 min the 500 or more measurements for the 18 elements in the samples are converted to percentage concentration; 7 min later the statistical analysis of the data is completed and the results typed out in convenient form.

On the punched cards that are used, each set of 4 successive columns represents a channel of information. Reading from the left, first is the sample identification code number (set manually) followed by 18 channels of measurements corresponding to 18 chemical elements; finally the last 4 columns record a serial number which is automatically advanced one digit for each run of the instrument.

Statistical results obtained from these data include: (1) An analysis of variance for each of the 18 elements with respect to locations in the metal; (2) the standard deviation of the method; (3) a listing of variances that are significant with respect to the standard deviation; (4) the coefficient of variation; and (5) maximum, minimum, and median values for each chemical element measured.

Creep of Nickel, Copper, and Nickel-Copper Alloys

A BUREAU study indicates that the creep resistance of nickel-copper alloys is superior to that of the parent metals. This conclusion is suggested by results obtained with high-purity nickel and copper and two nickel-copper alloys. Tests made in tension at high temperatures also reveal that the rate of strain hardening and degree of strain aging are increased by alloying the nickel and copper with each other. W. D. Jenkins and C. R. Johnson of the Bureau's thermal metallurgy laboratory carried out the investigation as part of a basic research program directed toward a better understanding of the properties of existing metals and alloys, and the development of improved materials.¹

At sufficiently high temperatures and stresses all metals creep; that is, they continuously deform under constant stress. Generally, creep takes place in three stages. In the first, there is a decreasing rate of extension; in the second, creep proceeds at a nearly constant rate; in the third, the creep rate increases, culminating in complete fracture. Structural changes accompany creep at elevated temperatures and the mechanical properties of metals are sensitive to the rate of straining. The creep-testing of metals in tension under varying stresses and temperatures can be used to assess the degree of this rate sensitivity.

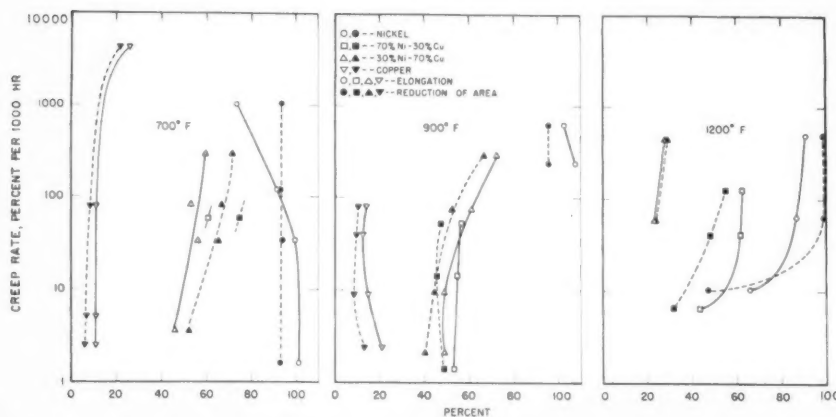
High-purity copper and nickel were selected for the current evaluation because they form with each other an unlimited series of solid solutions, and the two metals and their alloys have extensive industrial and defense applications. Tests were made at temperatures of 300°, 700°, and 900° F on initially annealed specimens of the two metals, and on a 70-percent-nickel—30-percent-copper alloy, and a 30-percent-nickel—70-percent-copper alloy. Tests at 1,200° F were also made on the nickel and the two alloys, but not on the copper because of its relatively low creep resistance at this temperature.

The specimens tested in creep were machined from an annealed rod of each material into round test bars of 0.505-in. diameter and 2-in. gage length. Each specimen was heated in air to the desired temperature and held at that temperature for 48 hr before loading. Equal increments of load were then added at 1-hr intervals until the desired creep stress was reached.

After plastic deformation started, the increment of strain was greater with each successive increment of stress at all temperatures; the strain values also increased with temperature. At each temperature and at equal strains, the strengths of the alloys were greater than those of the base metals. In addition, the differences in the rate of strain hardening between the metals and the alloys were strongly dependent on temperature.

Data derived from the tests made at 700° and 900° F indicate that the 30-percent-copper alloy was far more creep resistant than the 70-percent-copper alloy, regardless of the time under stress. The strengthening effects of alloying were more pronounced as the time at stress was increased and the temperature decreased. These observations were confirmed when the two alloys were tested at 1,200° F. If the major portion of the strengthening effects associated with alloying were due to lattice distortion, the magnitude of the differences between the two alloys would not have been so great. Apparently, some additional mechanism is partly responsible for this behavior.

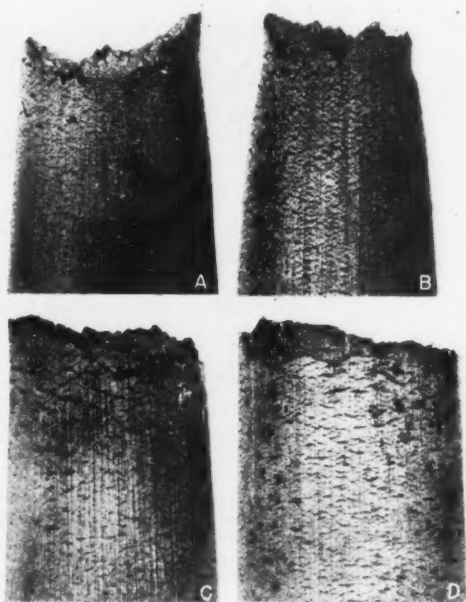
Various factors and mechanisms have been proposed to explain the initiation and propagation of creep in the third stage. These include: (1) Rising stresses resulting from a decrease in cross-sectional area of the specimen; (2) structural changes; (3) extensive recovery or recrystallization; (4) nucleation and density of void nuclei; and (5) growth of preexisting voids by vacancy condensation. To a limited extent, the data of the present study are consistent with all of these processes. When the tests were stopped prior to the third



Relation of second-stage creep rate to elongation and reduction-of-area values for specimens tested to fracture at different temperatures.

stage, no necking was observed and no voids were revealed at a magnification up to 2,000 diam. in any of the specimens. It was therefore concluded that necking and the growth of cracks are a consequence of creep in the third stage.

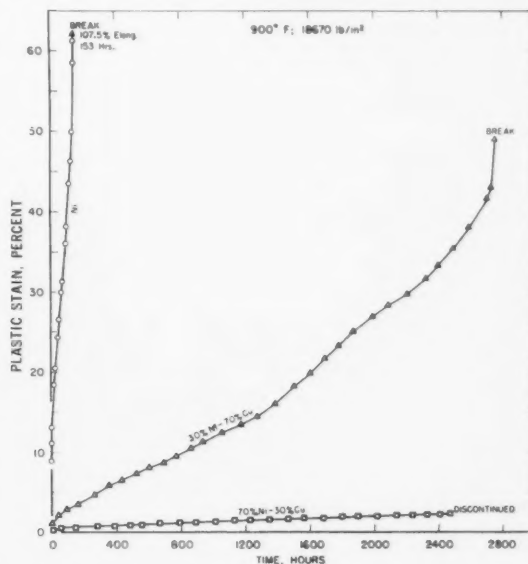
Two of the 30-percent-copper alloy specimens tested at 300° and 700° F exhibited the greatest tendency to necking in the third stage. They also tended to increase in hardness as the cross-sectional area decreased. However, on the three specimens of this alloy tested to fracture at 1,200° F, a softening effect with reduced cross section was noted. The tendency to soften with decreasing cross-sectional area was associated with high temperatures and low-creep rates. This behavior was accompanied by a progressively increasing number of microscopic cracks near the surface and in the interior of the specimens.



Four of the 30-percent-nickel—70-percent-copper specimens as they appeared after fracturing at different temperatures and at different rates (table below).

Specimen	Temperature	Second-stage creep rate	Reduction of area
	° F	Percent/1,000 hr	%
A	700	3.6	52
B	900	286	66
C	900	2.6	40
D	1,200	425	29

Data obtained after fracture of the nickel and the two alloys showed that the post-test hardness tended to increase with a decrease in test temperature (at a constant creep rate) or with an increase in creep rate (at a constant temperature). The same trend was noted in the copper specimens; however, the hardness values were relatively low and difficult to assess. Alloying the copper tended to raise the hardness values to a marked degree. With only one exception, the maximum hardness value for the high-purity nickel was higher than the corresponding values of the 70-percent-copper alloy.



Strain-time curves for nickel and two nickel-copper-alloy specimens tested at 900° F. All three of these specimens were stressed at 18,670 lb/in.².

For any specific creep rate and temperature, the elongation values for the alloys at complete fracture were intermediate between the high values for the nickel and the low values for the copper. The influence of creep rate on elongation and reduction-of-area values, however, was inconsistent and appeared to be a function of the test temperatures.

The experimental results obtained in this study demonstrated a lack of strict conformance to any of the known comprehensive theories on high-temperature deformation. This lack was attributed both to the initial structure of the specimens and to subsequent structural changes during creep.

¹ For further technical details, see Creep of annealed nickel, copper, and two nickel-copper alloys, by W. D. Jenkins and C. R. Johnson, *J. Research, NBS* **60**, 173 (1958) RP2836.

LEATHER

FUNGICIDES

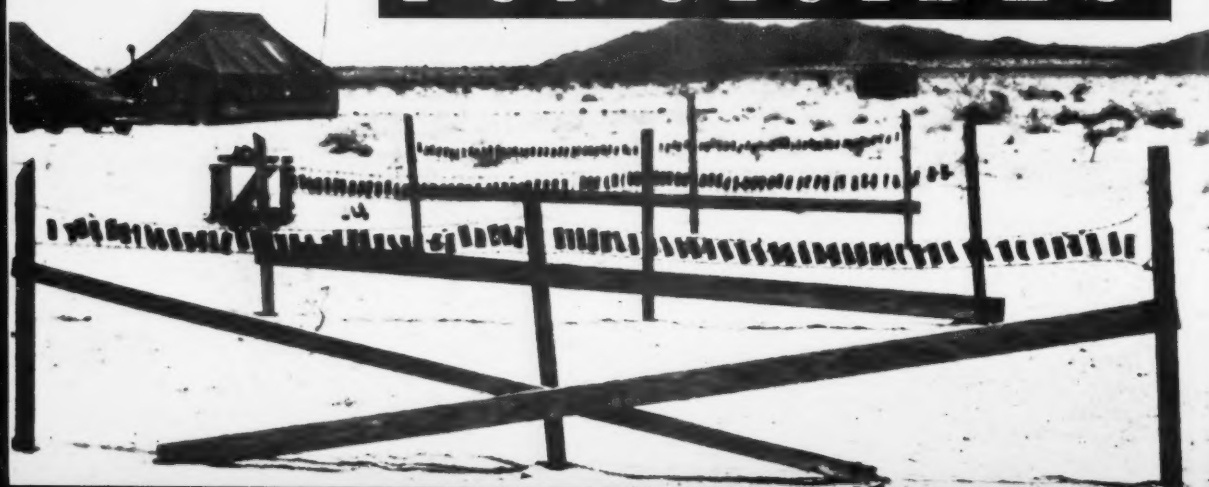
THE CHEMICAL STRUCTURE, endurance qualities, and deteriorating effects on leather of more than a hundred fungitoxic compounds have recently been studied by the Bureau in a research program sponsored by the Army Quartermaster Corps. One of the more interesting results obtained thus far is the discovery of two inert, colorless, and water-insoluble substances that have the unusual property of becoming poisonous to fungi only under mildew-growing conditions.¹ The two substances are bis(4-nitrophenyl) carbonate and bis(2-chloro-4-nitrophenyl) carbonate.

Prevention of mildew growth on leather items first became a serious problem to the military forces in World War II. Since then, experiments have shown that the main effect of mildew is the removal of greases from leather, causing stiffness and loss in tensile strength. Most tanning agents and lubricants required for finished leathers are mildew susceptible, and only a fungicide treatment of the leather will inhibit or prevent mildew growth. To satisfy military needs, a fungicide should give permanent protection against mildew; it should also be inexpensive, colorless, readily available, easy to apply, and harmless to human health and to leather.

As a result of earlier studies, Federal specifications were established in 1951 for a fungicide, 4-nitrophenol, to protect military footwear leathers. However, this compound has not been entirely satisfactory because of its color, solubility in water, and irritating skin effects under some conditions. The search for improved fungicides has therefore continued, with much of the work being performed by S. Dahl of the Bureau's leather laboratory and A. M. Kaplan of the Quartermaster Research and Engineering Center.

Nearly all of the compounds evaluated in the current investigation were known to be fungitoxic. Their relative effectiveness in leather was found (1) by exposure

Field-exposure sites used to evaluate fungicide treatments. Top to bottom, Panama Canal Zone, Savannah, Georgia, and Yuma, Arizona. (Top picture, U. S. Army photo.)



of specimens containing known percentages of the fungicides on mycelial mats of the fungus *Aspergillus niger*, and (2) by exposure in a tropical room at the U. S. Army Engineering Center, Fort Belvoir, Virginia.² As shown by an extensive field experiment, the latter test gives results that predict the performance of fungicides under the most severe mildew-growing conditions encountered in service.³

Deteriorating Effects

Even if a leather fungicide is highly potent as a mildew preventive, it is useless if it harms the leather itself.⁴ Careful attention was therefore given to this possibility in evaluating compounds as leather fungicides.

It has been shown that salts of copper and of iron are harmful to leather;⁵ and that leather deterioration is caused by small amounts of hydrochloric acid and by high concentrations of chloride, even in a neutral medium.⁶ The deteriorating action of inorganic materials containing copper or chlorine is well known, and a number of fungicides contain these elements. It would seem, therefore, that organic compounds containing these elements would also promote deterioration, either directly or by liberation of the respective ions.

However, it was found in this investigation that organically bound copper or chlorine are definitely less harmful to leather than are copper or iron ions. This result was obtained by evaluating the chlorine stability of chlorophenols and the effect of treatments with various fungicides—some of which contained copper or chlorine—on leather deterioration under accelerated-aging conditions. There are some indications that compounds containing organically bound copper or chlorine may not be completely harmless to leather, but they probably could be used as leather fungicides if they had the other required properties.

Chemical Structure

Earlier, the Prevention of Deterioration Center of the National Research Council had investigated the chemical structure as related to fungitoxic activity of many of the fungicides tested at the Bureau. But the relationship found in these studies did not always prevail when the fungicide was applied to leather. Besides the different responses of micro-organisms in different media, unknown alterations in the fungicide structure could be caused by reactions with the leather or with other substances used to treat the leather. A good leather fungicide would probably always show high potency against *Aspergillus niger* when added to a nutrient agar medium; but not all fungicides with high potency in agar or other substrates such as paint or textiles are good leather-mildew preventives.

Phenols, particularly the 4-nitro- and 4-thiocyanophenols, stand out thus far as the most effective of the many compounds evaluated as leather fungicides in the NBS program. Alkylation seems to decrease their effectiveness, while chlorination (for instance, as in 2-chloro-4-nitrophenol) seems to increase it.



Analytical method followed at the Bureau to determine fungicide concentrations present in leather. Fungicides that have been extracted with solvents from various leather specimens are being measured electrophotometrically.

Among compounds having a 2, 3, 5, 6-tetrachlorobenzene ring in common, but with different substituents on carbons 1 and 4, the most effective 1,4 combination found was $\text{OH}.\text{NO}_2$. Replacement of NO_2 in this combination with OH , Cl , and H , decreased the effectiveness in this order. Among aromatic nitro compounds without the tetrachloro structure, mildew-preventive activity was again associated with the 1,4- $\text{OH}.\text{NO}_2$ combination. Ethers of the phenols in both series of compounds were ineffective.

Permanence of Fungicides in Leather

Even though alteration of the original structure by reaction with the substrate may decrease fungitoxic potency, some fixation of the fungicide in the leather may help to increase its permanence. It can be demonstrated that some fungicides are lost from leather, under nonleaching conditions, probably by volatilization. A relatively nonvolatile fungicide might also be removed, especially under conditions favorable to mildew growth. Under such conditions, changes in temperature expose the leather to repeated cycles of condensation and evaporation of moisture that, in effect, constitute a process of steam distillation. The fungicide could be lost by this process if it is not fixed and possesses even a slight vapor pressure.

The military leather fungicide, 4-nitrophenol, is quite permanent in leathers under nonleaching conditions, probably because of a combination of relatively low volatility and fixation through hydrogen bonding. Evidence of fixation is found in the observation that 4-nitrophenol cannot be completely extracted from some leathers with chloroform unless water is present. This relative permanence in leather helps to explain the effectiveness of 4-nitrophenol as compared to other more fungitoxic materials.

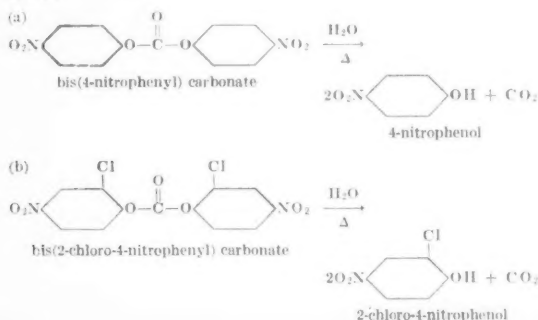


Leather specimens are examined for mildew-growth after several weeks' exposure to the tropical testing chamber at the U. S. Army Engineer Research and Development Laboratories, Ft. Belvoir, Va. (U. S. Army photo.)

The Bis Compounds

The current evaluation disclosed that bis(4-nitrophenyl) carbonate and bis(2-chloro-4-nitrophenyl) carbonate are about as effective as the corresponding nitrophenols; in the tropical room exposure approximately 0.3 percent (by weight) deposited in leather prevented mildew growth. These compounds are not readily volatilizable and are comparatively insoluble in water at room temperature. According to preliminary findings by the Office of the Surgeon General, U. S. Army, leathers treated with as much as 1.20 percent of the bis compounds were not irritating to human skin. Their effectiveness as leather fungicides is in contrast to the general inertness of similar compounds lacking a free phenolic OH group.

By an available analytical method,⁷ it was possible to establish the presence of 4-nitrophenol and 2-chloro-4-nitrophenol in leather that had been treated with the bis compounds and exposed to warm and humid conditions. The hydrolytic decomposition of the bis compounds to the free nitrophenols is represented as follows:



Apparently the effectiveness of the bis compounds is a consequence of their hydrolysis to nitrophenols. In the carbonate forms these compounds are probably inactive; such inactivity is evident in similar structures lacking a free hydroxyl group. Because the bis compounds are presumably less toxic to human skin than the phenols, their concentration in the leather would not have to be carefully controlled. Their hydrolysis to phenols is facilitated by conditions favorable to mildew growth, and conceivably takes place only under those conditions.

Stability characteristics of the bis compounds must be studied before their usefulness can be established. Tests are being made to ascertain whether they decompose appreciably in the vehicle used for their deposition in leather. In organic solvents such as chloroform, little if any decomposition occurs. However, in tannery applications organic solvents may not be feasible. Also, their rate of hydrolysis in leather under warm and humid conditions must be determined. Ideally, they should hydrolyze so slowly that the amount of phenols liberated would be equal to that lost by leaching under the same conditions. Consideration must also be given to their cost and availability.



A pair of boots after six months' exposure in the tropical testing chamber at Ft. Belvoir, Va. The boot at right had been treated with a bis compound; the boot at left was untreated.

¹ Studies of leather fungicides, by S. Dahl and A. M. Kaplan, *J. Am. Leather Chemists Assoc.*, **53**, 103 (1958).

² Fungicidal effectiveness of compounds applied to leather, by S. Dahl and A. M. Kaplan, *ibid.*, **52**, 536 (1957).

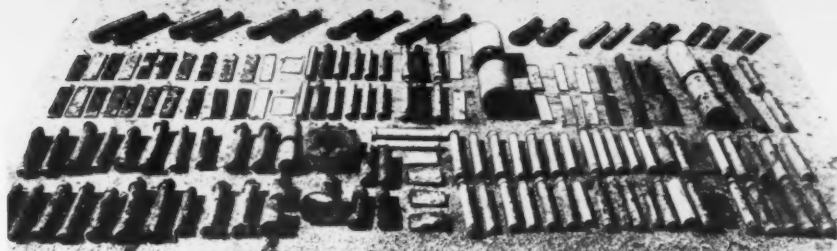
³ Laboratory and field exposure studies of leather fungicides, by S. Dahl and A. M. Kaplan, *ibid.*, **51**, 118 (1956).

⁴ The effects of fungicides on deterioration of leather, by S. Dahl, *ibid.*, **52**, 611 (1957).

⁵ Influence of copper and iron salts on the behavior of leathers in the oxygen bomb, by J. R. Kanagy, *ibid.*, **33**, 352 (1938).

⁶ See p. 698, *Modern practice in leather manufacture*, by J. A. Wilson, Reinhold Publ. Corp., New York (1941).

⁷ Some notes on the determination of para-nitro phenol, by R. M. Lollar, *J. Am. Leather Chemists Assoc.*, **45**, 728 (1950).



UNDERGROUND CORROSION

A Summary of 45 Years of Research

Current research on corrosion at the National Bureau of Standards emphasizes basic processes and principles. Two of the important current projects are conducted in cooperation with the Corrosion Research Council in their efforts to increase emphasis on the basic principles underlying corrosion. Since completion of the work described in the accompanying article, field studies have been confined to a few of the newer metals and alloys, such as titanium, stainless steels, copper-nickel alloys, and aluminum alloys that have recently come into use for underground structures.

Basic studies include further investigation of current and potential relationships, electrochemical polarization, and other electrical phenomena associated with corrosion. The chemistry of corrosion continues to receive major attention. One such study deals with the effects of adsorbed layers of moisture, presence of carbon dioxide, intensity of illumination, and other factors on corrosion re-

actions at the metal surface. Another study, part of the larger program on free radicals underway at the Bureau, is concerned with the effect of atomic oxygen on metals at low temperatures.

A somewhat different approach is the investigation of corrosion in large single crystals. By such experiments, a start has already been made in correlating corrosion with the arrangement of atoms in the crystal lattice. The importance of crystal structure has also appeared in work on stress-corrosion cracking, a particularly damaging type of failure resulting, as its name suggests, from the combined effects of stress and corrosion.

By attacking the problem from these various directions, it is hoped not only to improve still further the methods of combating corrosion, but to obtain information on basic properties of matter that have even wider areas of application.

RESEARCHES by the Bureau on the corrosion of underground structures, carried on for over 45 years, have been marked by steadily improved understanding of the causal factors at work and by the development of increasingly effective means of preventing the harmful effects that underground corrosion produces.¹ An important phase of the work, now essentially complete, has been an extensive field-burial program to determine the specific behavior of metals and coating materials when exposed for periods up to 17 years in a wide range of soil environments. At the same time, other phases of the corrosion program have led to increased information on the electrical and chemical aspects of the corrosion process, development of methods and instruments for measuring soil characteristics, improvements in the technique of cathodic protection, and virtual elimination of corrosion due to stray-current electrolysis.

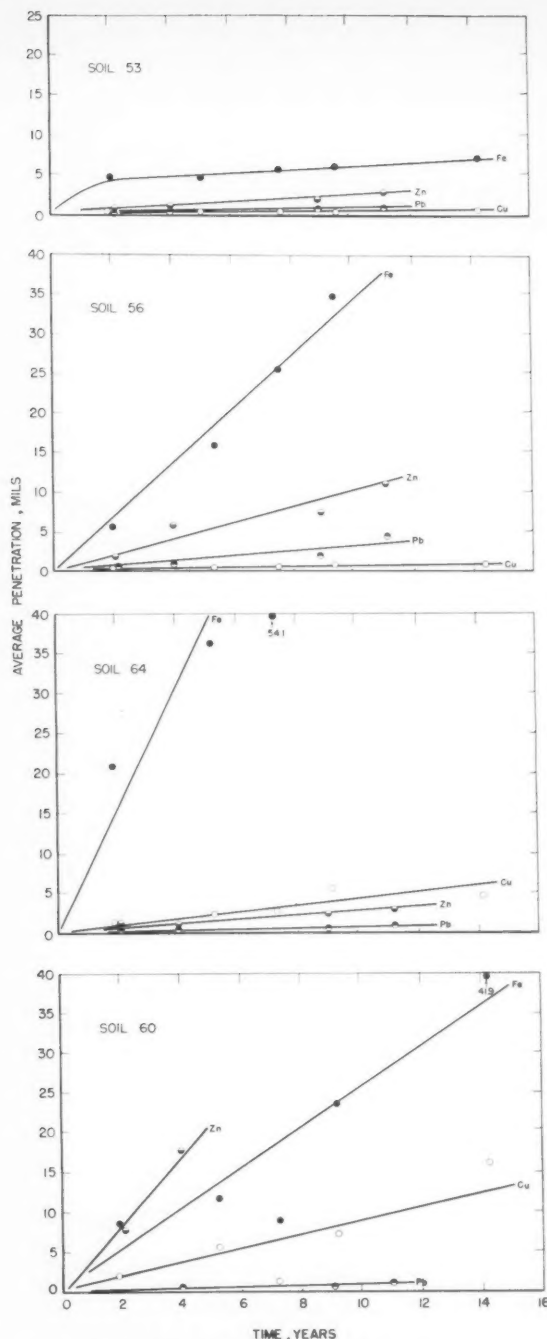
There are now in this country about 1 million miles of gas, water, and oil pipelines, 170,000 miles of buried power and communication cables, and an unknown number of tanks, pilings, burial vaults, and other struc-

tures. The annual cost to the U. S. pipeline industry alone, for protective measures and replacements due directly to corrosion, is estimated at 600 million dollars. A still higher indirect cost results from loss of products, service shutdowns, and loss of life and property by explosion and fire due to leakage from corroded pipes. Furthermore, since corrosion rates are often unknown, engineers have wasted large quantities of material by specifying unnecessarily large thicknesses in their designs.

Until about 35 years ago, underground corrosion was attributed solely to stray electric currents from external sources such as d-c powerlines and electric railways. Such currents pass through parts of underground structures and then discharge to the earth where conditions are favorable; corrosion occurs at the discharge areas.

The seriousness of the problem was recognized by the Congress in 1910, when the Bureau was authorized to

Photo above shows specimens removed from Hagerstown loam at Loch Raven, Md., after burial for periods up to 14 yr.



Comparison of corrosion behavior of iron (or steel), copper, lead, and zinc in 4 representative soil environments. Average depths of penetration depend on the time of exposure in each of the soils. Soil 53, well-aerated Cecil clay loam; 56, poorly aerated Lake Charles clay; 64, alkaline Docas clay; 60, Rifle peat having a high concentration of sulfate.

investigate the corrosive effects of stray currents and methods for combating them. In 10 years of field and laboratory studies, methods were developed that eliminated stray-current electrolysis as a major factor in underground corrosion.² Unexpectedly, however, these studies also showed that serious corrosion often occurred when stray currents were absent.

In 1922, therefore, a field burial program was initiated to determine the influence of various properties of soils on the corrosion of buried metals and to develop further methods for reducing corrosion losses. Data were obtained on nearly 37,000 specimens representing 330 varieties of materials. These were exposed for periods up to 17 years in 95 different types of soil at 128 test sites throughout the United States. The last specimens were removed in 1952, and several more years were required to analyze the data. The major field-burial program is now terminated; present work is confined to newly developed materials and the completion of several unfinished studies.

Meanwhile, electrical and electrochemical aspects of underground corrosion were continuously studied in the laboratory. The differential aeration cell developed by I. A. Denison, and modified by his coworkers, has been used to compare the corrosivities of different soils and of different metals in the same soil. Studies by W. J. Schwerdtfeger showed that the instantaneous rate of corrosion for ferrous metals in soils could be determined quantitatively from polarization characteristics of the metal.

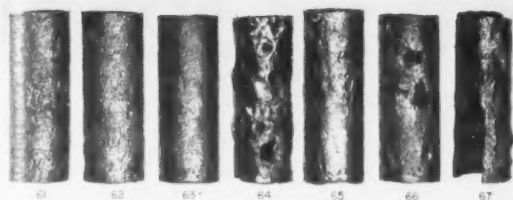
By-products of the investigation include a widely adopted inspection code for pipes and coatings, and the development of methods and instruments for measuring the electrical resistivity of soils in the field, such as the McCollum Earth Current Meter, the Wenner Four-Terminal Method, the Megger, and the extensively used Shepard Canes.

In the course of the field investigations, the Bureau had the cooperation of 17 technical and Government organizations, 103 manufacturers who supplied materials, and 105 utility companies and municipalities that provided test sites and labor.

Causes of Corrosion

Most underground corrosion is the result of electrochemical reactions. For such reactions to occur there must be a potential difference between two points of the metal in contact with an electrolyte. Current flows from the anode area through the electrolyte to the cathode and returns through the metal to complete the circuit. The anode area corrodes through loss of metal ions to the electrolyte.

Although this theory is easily understood, correlation of the theory with actual corrosion of metals underground is complicated because of the many factors that determine not only the amount or rate of corrosion, but also whether it is uniformly distributed over the metal surface, or is localized as the pitting type of corrosion. The pitting type of corrosion is especially damaging in pipelines and other structures that store or carry fluids;



Contrasting corrosion patterns produced by different soil environments on plain carbon steel buried for approximately 14 yr in each soil. Soil 61, Sharkey clay at New Orleans, La.; 62, Susquehanna clay at Meridian, Miss.; 63, tidal marsh at Charleston, S. C.; 64, Docas clay at Cholame, Calif.; 65, Chino silt loam at Wilmington, Calif.; 66, Mohave fine gravelly loam at Phoenix, Ariz.; and 67, cinders at Milwaukee, Wis.

but for load-bearing structures, such as piles, the main concern is with over-all loss in weight or strength.

The chief contributing factors are the presence of moisture, oxygen and soluble salts in the soil, and the permeability of the soil to these substances. Moisture provides the soil electrolyte which is composed of hydrogen and hydroxyl ions from the water itself, and a variety of ions from the salts dissolved from the soil. These ions determine the electrical resistivity, as well as the chemical properties of the soil. Oxygen, from the air or from oxidizing compounds in the soil, stimulates corrosion by combining with metal ions. If the resulting corrosion products are soluble or otherwise removed from the anodic areas, corrosion proceeds; if they accumulate, they may protect the metal against further corrosion or, if they are more cathodic than the bare metal, they will accelerate and localize the corrosion.

Other factors that determine the amount of current that flows from metal to soil are the size, number, and location of anodic areas. Galvanic corrosion may result because of contact between dissimilar metals, and because of local differences in the packing of the soil which may produce oxygen concentration cells; the regions with less oxygen are anodic with respect to those with more.

Bacteria must also be considered, particularly the anaerobic sulfate-reducing bacteria that convert soluble sulfates to sulfides. These are most active in poorly aerated swamp areas where the pH of the soil water is about neutral and there is enough organic matter and soluble sulfates for the organisms to thrive.

Soils and Burial Procedure

The 95 soil types used in the field program show wide differences in physical and chemical properties. In texture, the soils vary from soft, spongy peats through soft clays, loams, and silts to coarse-grained sands and gravels. The resistivity ranges from 51 ohm-cm. approximately that of sea water, to a value over 1,000 times larger, indicating the absence of soluble salts. Chemically, the soils range from extreme acidity ($\text{pH}=2.6$) to high alkalinity ($\text{pH}=10.2$), and from

highly oxidizing to definitely reducing. In addition, there are striking differences in the kinds and amounts of soluble salts present.

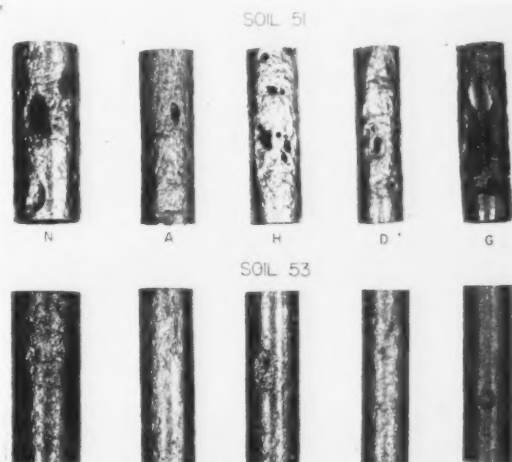
In the first extensive burials (1922), specimens of commonly used ferrous pipe materials were buried at 47 test sites. In 1923, similar ferrous materials and some copper and copper alloys were buried in a new group of sites; and a burial program was also started on bituminous coatings. Between 1932 and 1941 additional burials were made of low- and high-alloy irons and steels, copper and copper alloys, zinc, alloys of lead, lead-coated steels, galvanized iron, tin-coated copper, various nonbituminous organic coatings, and asbestos cement pipe.

As a rule, 10 or 12 specimens of each material were buried at each site, and 2 specimens were removed periodically, so that corrosion data were obtained for maximum exposures of 12 to 17 years for all materials. Specimens were usually placed in a single row and were arranged so that 2 samples of each material could be removed without disturbing the specimens still in the ground. Exhumed specimens were treated in the Bureau's corrosion laboratory by chemical and mechanical procedures to remove the corrosion products without significant loss in weight or mechanical injury to the uncorroded metal. Measurements of weight loss and pit depth were then made.

Plain Ferrous Metals

The plain ferrous pipe materials represented in the field tests were open-hearth iron and steel, hand-puddled and mechanically puddled wrought iron, Bessemer

Corrosion patterns on specimens exposed for 14 yr to very corrosive Acadia clay (soil 51) at Spindeltop, Tex., and to moderately corrosive Cecil clay loam (soil 53) at Atlanta, Ga. Note the similar patterns produced in different metals by the same soil. N, plain carbon steel; A, wrought iron; H, copper-molybdenum open-hearth iron; D, 2-percent nickel, 1-percent-copper steel; G, plain cast iron.



steel, plain-carbon steel, pit-cast and centrifugally-cast iron.

The field test results for these metals, as well as those for low-alloy steels, exhibit very clearly the controlling influence of the soil on the character of the corrosion. All the plain ferrous materials showed similar corrosion patterns when buried in the same soil, but the type of corrosion varied widely in different soils. In general, a high initial corrosion rate, decreasing after a few years to almost complete cessation, is found in well-drained soils with high resistivities; while the corrosion rate is nearly constant after the first year or two in poorly drained soils with low resistivities.

Alloy Steels and Irons

Data were obtained on the following low-alloy steels: Copper-bearing steel; copper-molybdenum open-hearth iron; nickel-copper steels; and steels containing from 1- to 6-percent chromium with and without molybdenum.

The general effect of the alloying elements was to lower the initial rate of weight loss, but to increase the initial rate of pitting, as compared with plain carbon steel. Except in very poorly aerated and reducing soils, however, the pitting rate diminished more rapidly for the alloy steels than for plain steels. Chromium and molybdenum were particularly effective in reduc-

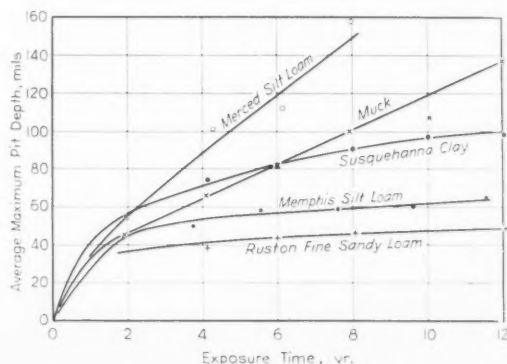
Corrosion test specimens being buried in Hagerstown loam at Loch Raven, Md., one of 125 sites throughout the country used in field studies of underground corrosion. The specimens were usually arranged, as shown here, in a single trench.



ing the corrosion of low-alloy steels in the most corrosive site, a cinder fill.

The higher-alloy steels tested contained up to 8-percent chromium, with and without nickel and molybdenum. Increasing the chromium content caused a gradual decrease in weight loss, but pitting was accelerated by additions of chromium beyond 6 percent. The tendency of high concentrations of chromium to accelerate pitting appears to be neutralized by adding sufficient nickel to produce steels of the austenitic type.

Field tests on low-alloy cast irons, containing up to 3 percent of nickel with and without copper, showed that the presence of such amounts of nickel or copper had no significant effect in any of the soils up to the amounts used. Austenitic cast iron was considerably more resistant to corrosion than plain cast iron.



Depth of corrosion pits formed in plain carbon steel after burial for various periods in different soils. Curves show that in well-drained soils having high electrical resistivities, such as Ruston fine sandy loam and Memphis silt loam, the corrosion rate may be high, initially, but decreases considerably after a few years; while in poorly drained soils with low resistivities, such as Merced silt loam and muck, the corrosion rate is nearly constant after the first year or two. Similar results were found for other plain ferrous metals.

Copper, Brass, and Lead

Results on copper and copper alloys indicate that tough-pitch copper, deoxidized copper, copper containing up to 3 percent of silicon with and without tin, and red brass (15-percent Zn) all behave essentially alike. Soils, including cinders, with high concentrations of sulfides, chlorides, or hydrogen ions were found the most corrosive toward these materials.

The corrosion rate of Cu-Zn alloys with more than 27-percent zinc increased approximately as the amount of zinc and was generally accompanied by dezincification—except in soils with moderate or high concentrations of sulfide. In the sulfide soils the corrosion rate decreased with greater zinc content and dezincification did not occur.

Specimens of 3 high-alloy steels after exposure in 3 different soils for 14 yr, showing the effect on corrosion of both the specimen composition and the soil environment. U, 12-percent-chromium steel; V, 18-percent-chromium steel; W, 18-percent-chromium, 9-percent-nickel steel. Soil 64, Docas clay; 65, Chino silt loam; 66, Mohave fine gravelly loam.

Chemical, antimonial, and tellurium lead showed no appreciable differences in corrosion behavior. The corrosion rate of each tends to increase with decreasing aeration of the soil. Organic acidity was corrosive; but in soils high in sulfates, chlorides, or carbonates, the corrosion products formed a protective coating.

Metals Compared

To compare the corrosion resistances of plain iron and steels, copper, lead, and zinc, the soils were divided into 4 groups: well aerated, poorly aerated, alkaline, and high in sulfide or sulfate. When corrosion-time curves were plotted for specimens buried in representative soils of these types, it was found that plain iron or steel corroded much more rapidly than the other metals in all the soils except the one high in sulfate. In this soil zinc corroded more than steel; but only lead could be expected to withstand for long the corrosive action of such a soil.

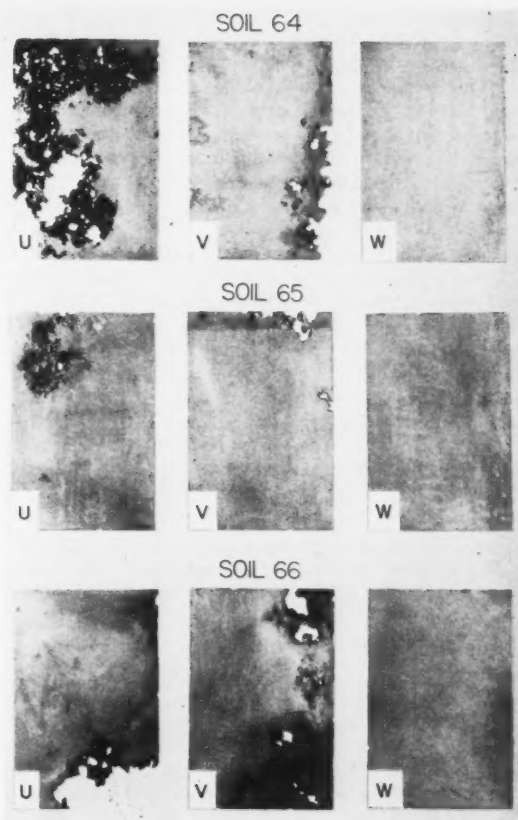
In the well-aerated and poorly aerated soils that are representative of most of the United States, copper showed the highest corrosion resistance. This superiority is especially marked in the poorly aerated environment, where the corrosion rates of iron or steel, zinc, and lead are proportional to time. In the well-aerated environment, the rates of corrosion of the same metals decreased rapidly with longer periods of exposure.

Coatings, Asbestos-Cement Pipe

Field tests on galvanized coatings over iron and steel showed that a 2-oz/ft² coating of zinc was sufficient protection in inorganic oxidizing soils, 3-oz/ft² was needed in inorganic reducing soils, and still heavier coatings in high-reducing organic soils. For steel coated with lead and copper coated with tin, both by the hot-dip process, it was found that in a great many soils the local corrosion is much deeper than the thickness of generally available commercial coatings.

Coatings of vitreous or porcelain enamel revealed no signs of deterioration in 14 years' exposure. Baked phenolic coatings showed marked superiority to air-dried phenolic coatings in preventing pit formation in the underlying steel. Rubber and rubberlike coatings were also very successful, mainly because of their large thicknesses. Numerous other organic coatings failed to give adequate protection because of insufficient thickness or unsatisfactory bonding between metal and coating.

Extensive field tests were made on all bituminous coating materials commercially available (1929-1932), including shields, wrappings, and reinforcing materials. As a result of these experiments, performed with



the cooperation of the American Gas Association and the American Petroleum Institute, improved methods of applying the coatings were developed, many previously used coatings were removed from the market, and new specifications for bituminous coatings were adopted by the industry.

Pipes of asbestos-cement, now widely used for transporting water, were exposed for periods of up to 13 years. In general, the data show an increase in strength during the first few years, a result due to the curing process that cement products normally undergo in moist atmospheres. However, after completion of this curing period there was a loss in strength, a decrease in apparent specific gravity, increased water absorption, and some softening of the surface. These effects were accelerated by both organic and inorganic acidity in the soils.

Cathodic Protection

Since the early 1930's, the method of cathodic protection has come into more and more extensive use as an alternative or supplement to protective coatings. The method consists in impressing electromotive forces on the underground structure so that the entire struc-

ture remains cathodic to the soil at all times. This prevents positive metal ions from passing into solution, and thus blocks the corrosion reaction.

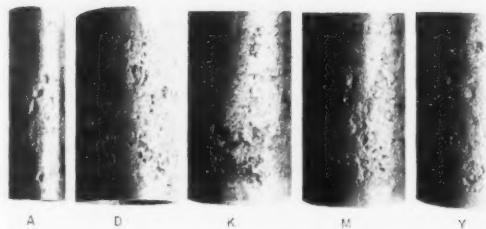
If electric power is available, it is converted to dc (if not already in that form) and auxiliary anodes of scrap iron, graphite, or other materials are used to carry the current into the earth. Where power is not easily available, aluminum, magnesium, or zinc are used as sacrificial anodes to supply the needed emf by galvanic action.

Experimental and theoretical investigations by the corrosion laboratory have contributed to cathodic protection technique since its early development. For example, studies were made that helped determine which soil conditions are favorable for the use of zinc sacrificial anodes.

³A comprehensive survey of Bureau research in this field is given in NBS Circular 579, *Underground corrosion*, by M. Romanoff (1957), available at \$3.00 per copy from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

⁴This work is summarized in NBS Circular 579.

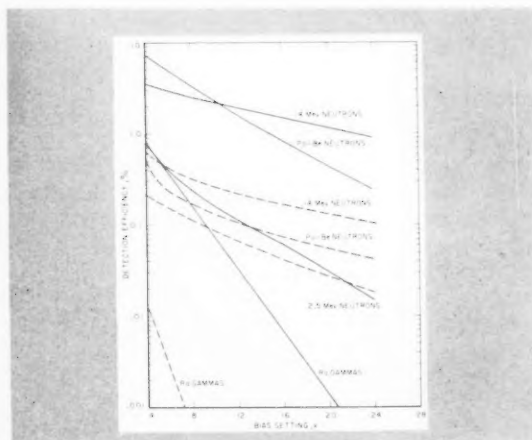
Note on references: A list of publications on underground corrosion, cathodic protection, and stray-current electrolysis, including selected articles by staff members in outside journals, is given in List of Publications LP7, copies of which can be obtained from the Publications Section, National Bureau of Standards, Washington 25, D. C. The bibliography in NBS Circular 579 (see footnote 1, above) contains a more complete list of Bureau articles in outside journals and includes references to work of



Similar corrosion patterns on different wrought metals exposed to the same soil (Hempstead silt loam) for approximately 12 yr. A, open-hearth iron; D, wrought iron; K, open-hearth steel; M, Bessemer steel; and Y, open-hearth steel with 0.2-percent copper.

other laboratories. Descriptive summaries of various phases of underground corrosion research at the Bureau are given in the following NBS Technical News Bulletin articles: Laboratory measurements of corrosion in soils **38**, 13 (1954); Electrical measurement of corrosion rate **37**, 22 (1953); Corrosion of low alloy irons and steels in soils **37**, 151 (1953); Corrosion of nickel cast irons in soils **38**, 160 (1954); Corrosion of galvanized steel underground **37**, 76 (1953); Cathodic protection of steel underground **36**, 1 (1952); Cathodic protection of underground structures **32**, 85 (1948).

IMPROVED METHOD FOR NEUTRON DETECTION



Increased efficiency of Bureau-developed plastic phosphor-in-plastic buttons over the older inorganic zinc sulfide-phosphor-in-plastic type. Solid lines represent response of a 3-percent concentration by weight of organic scintillator in polystyrene. Dotted line shows response of a 30-percent concentration by weight of ZnS in lucite.

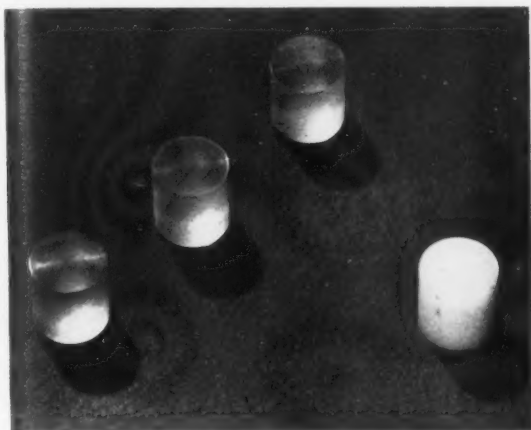
THE BUREAU has recently made improvements in both the speed and efficiency of a widely used scintillation method for neutron detection.¹ This method makes use of a plastic button containing an indicating compound which emits a light pulse when activated by incident particles. By substituting organic plastic scintillators for the inorganic phosphors previously used as indicators, B. Brown and E. B. Hooper, Jr. have obtained a button that has advantages for many problems in neutron detection and which also shows potentialities for use as a neutron dosimeter for all energies of neutrons.

In the scintillation process, an ionizing particle excites an atom by raising its electrons to a higher energy state. Photons are then emitted, causing a light pulse, and the electrons return to their normal state. Since neutrons are uncharged they can be detected only by the action of secondary particles. Thus, the success of the button detectors is due to the supply of protons present in the plastic medium. These are set into motion by the incident neutrons, and produce pulses. Because the proton-produced pulses are much larger than pulses produced by the secondary electrons from background gamma radiation, excellent discrimination is

obtained. This feature—not available with many other detectors — has led to the widespread use of plastic buttons.

The efficiency of the older phosphor-in-plastic detectors is proportional to the concentration of phosphor (ZnS) up to about 30 percent by weight. This limits the number of phosphor particles available for proton collisions because thick buttons become opaque. Neutron pulses are then attenuated and efficiency is adversely affected.

The use of organic plastic scintillators in the plastic medium yields a transparent button which can be made much thicker and therefore more efficient than the older type of button. Neutron detection efficiencies were found to be roughly 10 times greater in the newly de-



Phosphor-in-plastic neutron detectors. All buttons shown contain 5-percent phosphor by weight. Buttons left to right contain as phosphors KI (TI), Pilot B, Scintilon, and ZnS (Ag). The ZnS button is comparatively opaque.

veloped detectors. This improvement in efficiency is obtained even though the concentration by weight of the plastic phosphor must be kept below 5 percent to prevent loss in discrimination ability.

To make the new-type button, commercially available plastic phosphors are mixed with either lucite or polystyrene particles and the mixture is molded in a heated hydraulic press. Buttons made with very small particles (44 to 177 μ in diameter) were found to have both higher neutron detection efficiency and better gamma-ray discrimination than pellets made with larger particles (200 μ). Particles of the desired size were obtained by grinding and sifting lathe shavings.

To employ the button as a scintillation counter, it is necessary only to couple it by silicone oil into a photomultiplier tube, since the transparent plastic transmits light pulses. In NBS experiments the photomultiplier signal was fed through a preamplifier and linear amplifier into a multichannel analyzer to obtain pulse-height spectra. Buttons were tested at neutron energies of 2.5, 4.5, and 14 Mev; detection efficiencies were found to decrease at lower energies. Such low-fluorescence efficiency is characteristic of all organic scintillators for low-energy neutrons. Thus at energies below 1 Mev, where the inorganic phosphors still produce large light pulses, they are more efficient than the organic scintillators. At all higher energies the plastic phosphor buttons were more efficient than any inorganic phosphors tested. By combining a plastic phosphor and an inorganic crystal, such as thallium-activated sodium or potassium iodide, in a single button, it may be possible to obtain a device suitable for neutron dosimetry applications.

¹ Phosphor-plastic matrix for fast neutron detection, by B. Brown and E. B. Hooper, Jr., *Nucleonics* **16**, 96 (April 1958).

Publications of the National Bureau of Standards

Periodicals

Journal of Research of the National Bureau of Standards, Volume **61**, No. 2, August 1958 (RP2886 to RP2893 incl.) 60 cents. Annual subscription \$4.00, \$1.25 additional for foreign mailing.

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SINCLAIR WEEKS, *Secretary*
NATIONAL BUREAU OF STANDARDS
A. V. ASTIN, *Director*

September 1958 Issued Monthly Vol. 42, No. 9

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H. Shoub and T. G. Lee. 6th Symposium on Combustion (1957).

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Patents

(The following patents were granted to NBS inventors during the quarter ending June 30, 1958, and were assigned to the U. S. Government as represented by the Secretary of the Department noted in parentheses.)

- No. 2,831,326. April 22, 1958. Valve. Robert J. Richards and Robert B. Jacobs (Commerce).
- No. 2,834,922. May 13, 1958. Cellular method of electronic assembly. Paul J. Selgin (Navy).
- No. 2,835,801. May 20, 1958. Asynchronous-to-synchronous conversion device. Ruth C. Haueter (Commerce).
- No. 2,835,816. May 20, 1958. Adjustable low inductance capacitor with separately rotatable slotted discs for tracking adjustment. Gustave Shapiro and James R. Feler (Navy).
- No. 2,838,426. June 10, 1958. Mildew-proofing of leather. Sverre Dahl (NBS) and Arthur M. Kaplan (QMC) (Commerce).
- No. 2,839,998. June 24, 1958. Inertia and air-operated arming mechanism. Jacob Rabinow, Laurence M. Andrews, and John W. Bowling (Army).
- No. 2,840,743. June 24, 1958. High vacuum gimbals. Ladislaus L. Marton, Roald A. Schrack, and John A. Simpson (Air Force).
- No. 2,840,799. June 24, 1958. Very rapid access memory for electronic computers. Arthur W. Holt (Commerce).

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